OZONE-FRIENDLY FLUID

The present invention relates to a composition of fluids for use in refrigeration systems (RS) and also in heat pumps (HP), and it is to be used in low-capacity units.

A known two-component azeotropic fluid contains 1,1,2,2-tetrafluoroethane (R134) and butane in various molar ratios [1].

However this mixture has a relatively low volumetric refrigeration capacity and a high normal boiling point, which cause vacuum in the RS evaporator at temperatures below 250 K.

Another known two-component propellant and refrigerant contains trifluoropropylene ($C_3H_3F_3$) and propane or ethylene, or n-butane, or isobutane, or a mixture thereof [2]. The content of trifluoropropylene (R1243) in the mixture is 1 to 91 by mass of the mixture.

The known refrigerant which contains propane or ethylene as hydrocarbon is mainly deficient to use because of elevated absolute pressure values of the forward flow and return flow, which does not make it possible to use the refrigerant directly in existing RSs and HPs. Binary mixtures of E1243 with n-butane or isobutane have a relatively low volumetric refrigeration capacity and relatively high normal boiling point.

The closest prior art for a refrigerant according to the invention in terms of composition is a three-component fluid containing tetrafluoroethane and hydrocarbons which may be represented, e.g., by propane and fluoromethane and fluoroethane, i.e., by fluorinated hydrocarbons, with tetrafluoroethane being

used in quantities of 25 to 95 mole by weight in different examples [3].

However, this refrigerant is deficient because of the increased absolute pressure values of the forward and return flows, which hampers its direct use in existing RSs and HPs.

It is an object of the invention to improve the volumetric refrigeration capacity of the fluid and also to lower the normal boiling point in the RS evaporator to a level below 250 K.

The above object is accomplished by the fact that in an ozone-friendly refrigerant containing three components: tetrafluoroethane, a fluorinated hydrocarbon, and a hydrocarbon having three to five carbon atoms, the fluorinated hydrocarbon is an unsaturated fluorinated hydrocarbon from the propylene series, having a structural formula $C_3F_nH_{(6-n)}$, wherein n is one to six, with the following proportioning of the components: tetrafluoroethane 1 to 94 mole, an unsaturated fluorinated hydrocarbon 1 to 94 mole, and a hydrocarbon 5 to 80 mole.

In preferred embodiments of the invention, the hydrocarbon may be a pure substance: propane, or propylene, or n-butane, or isobutane, or n-pentane, or isopentane, or may be in the form of a binary mixture of propane and propylene, or n-butane and isobutane, or n-pentane and isopentane, or other hydrocarbons with appropriate boiling point values, and it is preferred and necessary that when binary mixtures of different hydrocarbons are used the total quantity of the hydrocarbon components in moles should correspond to the above-specified hydrocarbon molar composition of the fluid with any proportioning of the hydrocarbons in the mixtures.

Advantages of the fluids according to the invention will be discussed in detail in the following preferred exemplary embodiments, which do not, however, limit the spirit and scope of the invention as defined in the claims provided below.

Example 1. A fluid according to the invention was prepared using weight ratios. Each component of the mixture was stored in a separate bottle. Each of the bottles was connected in turn to a set-up, and a quantity of the component that was released into the overall receiver had the mass that corresponded to the preset quantity of the component in the fluid expressed in mole percent.

First, the high-boiling component, which had the lowest saturation pressure at a given temperature, more specifically, a hydrocarbon, was released into the receiver. Then components having a lower normal boiling point ($T_{n.b.p.}$) and hence a higher vapor pressure were added. As shown in Tables 1, 2, tetrafluoroethane or an unsaturated fluorinated hydrocarbon of the propylene series was supplied first, with the priority given to the component having a higher boiling point.

Example 2. When propane or propylene was used as the hydrocarbon, the supply sequence was changed. It was either tetrafluoroethane or an unsaturated fluorinated hydrocarbon of the propylene series (Table 1) that was released first, and the component having a higher boiling point was given priority. The lower-boiling hydrocarbon component was then added.

The minimum hydrocarbon content (5%) and the maximum hydrocarbon content (80%) in the mixture was determined in such a manner as to achieve the maximum possible volumetric refrigeration capacity of the mixture when a high-boiling hydrocarbon such as, for instance, n-pentane and a low-boiling hydrocarbon such as, for

instance, propane were used in the mixture (Figs. 1, 2). The peak of the volumetric refrigeration capacity in mixtures containing tetrafluoroethane and an unsaturated fluorinated hydrocarbon such as $C_3F_nH_{(6-n)}$ hydrocarbon is explained by the quasi azetropic compositions. When such mixtures are used, the suction pressure and the refrigerant density increase at the compressor inlet, which in turn results in RS or HP refrigeration capacity being increased with the same energy efficiency.

The ratio of tetrafluoroethane to a $C_3F_nH_{(6-n)}$-type fluorinated hydrocarbon in the mixture is chosen based on the maximum energy efficiency with the pre-set volumetric refrigeration capacity.

The choice of the composition of the three-component fluid within the above-specified limits is made in such a manner as to make sure that the pressure in the evaporator does not go below the atmospheric pressure at the desired temperature level. The mixture phase equilibrium data is used to check for this condition.

The use in the fluid of tetrafluoroethane and a $C_3F_nH_{(6-n)}$-type unsaturated fluorinated hydrocarbon, which have relatively low normal boiling points (Tables 2, 1), allows the fluid boiling point to be reduced below 250 K while avoiding vacuum in the RS evaporator.

At the same time, the volumetric refrigeration capacity of the mixture increases with the energy efficiency of the RS remaining the same. Table 3 shows comparative characteristics of a non-regenerative single-stage RS, using a conventional refrigerant R12, 1,1,2,2-tetrafluoroethane (R134a), an R134-butane mixture (prior art), and the fluid according to the invention comprising 1,1,1,2-tetrafluoroethane (R134a) and trifluoropropylene (R1243). The characteristics are given for operation of small refrigerators:

condensation point T_c=313 K (+40°C) and boiling point T_e=250 K (-23°C).

Table 4 shows similar characteristics for a theoretical cycle of a single-stage regenerative vapor-liquid RS. The regeneration ratio is assumed at 20 K.

It can be seen from the Tables that the fluid according to the invention offers a higher volumetric refrigeration capacity with the same energy efficiency and pressure differential in the RS when compared to the prior art.

Patent claims:

1. Ozone-friendly fluid, comprising three components in the form of tetrafluoroethane, a fluorinated hydrocarbon, and a hydrocarbon having 3 to 5 carbon atoms, characterized in that the fluorinated hydrocarbon is an unsaturated fluorinated hydrocarbon from the propylene series, having a structural formula $C_3F_nH_{(6-n)}$, wherein n is 1 to 6, with the following proportioning of the components in the mixture in moles:

Tetrafluoroethane 1 to 94
Unsaturated fluorinated hydrocarbon 1 to 94
Hydrocarbon 5 to 80

2. Fluid according to Claim 1, characterized in that the hydrocarbon is a pure substance: propane, or propylene, or n-butane, or isobutane, or n-pentane, or isopentane.

3. Fluid according to Claim 1, characterized in that the hydrocarbon is in the form of a binary mixture of propane and propylene, or n-butane and isobutane, or n-pentane and isopentane.

Table 1

Unsaturated Fluorinated Hydrocarbons of the Propylene Series

Substance	Structural formula	Normal boiling point, K	Transition point, K	Critical pressure, atm.
R1216	$CF_3CF{=}CF_2$	244.1	359.2	31.0
R1225	$CF_3CH{=}CF_2$	252.5	380.6	37.8
R1234	$CH_2{=}CFCF_3$	244.9	370.4	33.1
R1243	$CF_3CH{=}CH_2$	247.7	378.2	37.5
R1252	$CF_2{=}CHCH_3$	245.2	378.3	39.4
R1261	$CH_2{=}CFCH_3$	249.2	388.7	42.9

Table 2

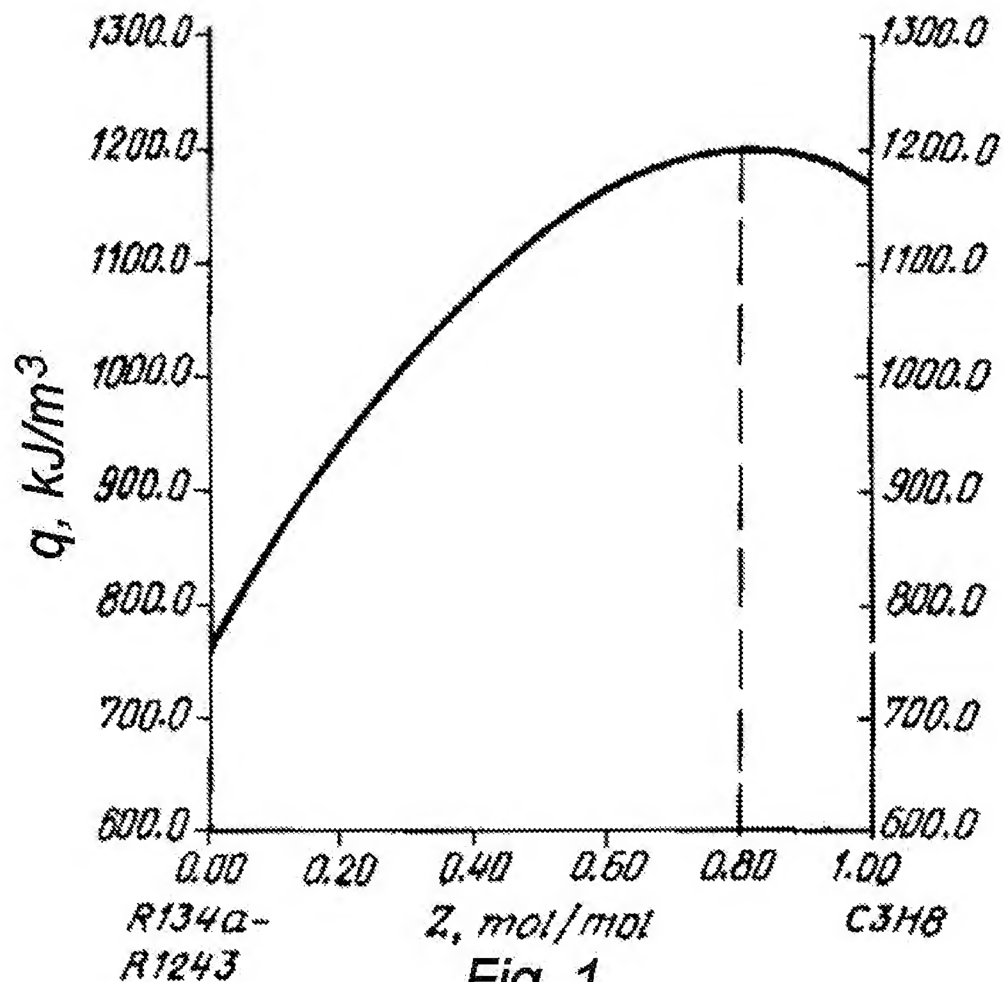
Substance	Normal boiling point, K	Transition point, K	Critical pressure, atm.
1,1,2,2-tetrafluoroethane (R134)	253.7	383.4	37.2
1,1,1,2-tetrafluoroethane (R134a)	246.7	373.8	40.0

Table 3

Refrigerant	Return flow pressure, atm.	Pressure ratio	Vol. refrigeration capacity, kJ/m^3	Energy efficiency, %
R12	1.3	7.3	830	25
R134a	1.2	9.0	758	22
R134 (0.66)-isobutane (0.34)	1.1	8.3	687	22
R134a (60 mole%)-R1243 (10 mole%)-Isobutane (30 mole%)	1.5	7.7	843	22

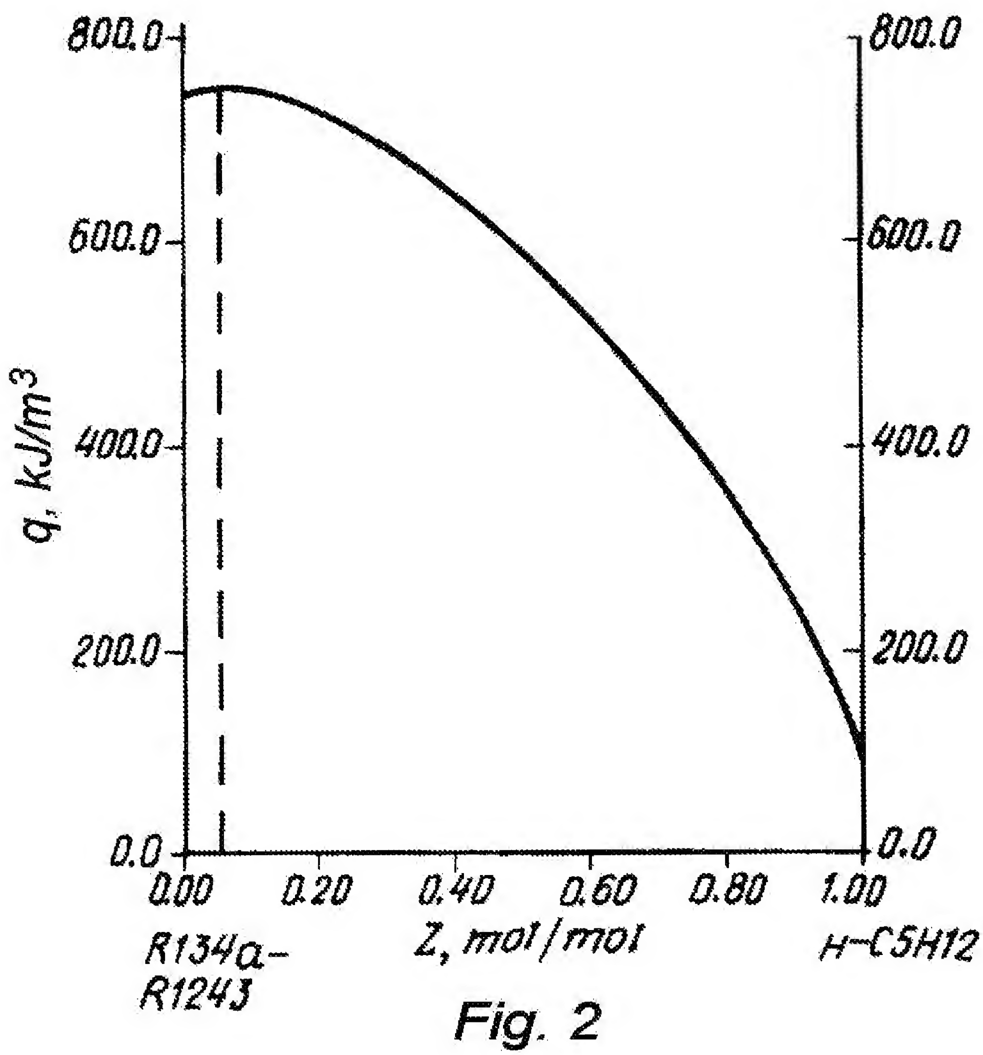
Table 4

Refrigerant	Return flow pressure, atm.	Pressure ratio	Vol. refrigeration capacity, kJ/m^3	Energy efficiency, %
R12	1.3	7.3	847	25
R134a	1.2	9.0	782	23
R134 (0.66)-isobutane (0.34)	1.1	8.3	717	23
R134a (60 mole%)-R1243 (10 mole%)-Isobutane (30 mole%)	1.5	7.7	889	23



1300.0
1200.0
1100.0
1000.0
900.0
800.0
700.0
600.0
q, kJ/m3
0.00
0.20
0.40
0.60
0.80
1.00
R134a-
R1243
Z, mol/mol
C3H8

Fig. 1



800.0
600.0
400.0
200.0
0.0
q, kJ/m3
800.0
600.0
400.0
200.0
0.0
0.00
0.20
0.4D
0.60
0.80
1.00
R134a-
R1243
Z, mol/mol
H-C5H12

Fig. 2